

# Chromium Etchant

## Standard Operating Procedure

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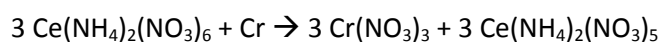
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### 1. Purpose and application

Chromium etchants typically are mixtures of perchloric acid ( $\text{HClO}_4$ ), and ceric ammonium nitrate  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ . Perchloric acid is a very strong acid and therefore almost completely dissociated in aqueous solutions ( $\text{pK}_s < -8$ ), and serves for chemically stabilizing the ceric ammonium nitrate. Ceric ammonium nitrate itself is a very strong oxidizer.

The following chemical equation summarizes the mechanism of chromium etching with perchloric acid and ceric ammonium nitrate:



Chromium nitrate steadily produced during etching forms a dark film on the chromium surface and - due to its aqueous solubility - is dissolved in the etchant.

Copper, silver and vanadium are strongly etched by this etchant, while aluminium, titanium, tungsten and nickel show a comparable low etch rate. The noble metals gold, platinum and palladium are not attacked.

Etching temperature varies depending on film thickness. At 25°C, the Cr will etch at a rate of approximately 60 nm/min [1].

### 2. Equipment, Chemicals and Supplies

Chromium etchant is composed out of three chemicals:

1. 10.9 wt.% Ceric ammonium nitrate
2. 4.25 wt.% Perchloric acid
3. 84.85 wt.% Water

Mixture is purchased from Microchemicals.

[https://www.microchemicals.com/products/etching\\_mixtures/technietch\\_cr01chromium\\_etchant.html](https://www.microchemicals.com/products/etching_mixtures/technietch_cr01chromium_etchant.html)

### 3. Personal Protective Equipment (PPE)

The following equipment should be used:

- Eye protection: Safety glasses, (optional with face shield).
- Protective gloves: Black neoprene gloves. Check gloves for leaks before use.
- Protective clothing or equipment: Apron.

### 4. Operational Procedures

1. Get three glass beakers or envelopes which will fit your sample and place them in the bench.
2. Write down your name and type of chemical for every beaker/envelope.
3. Carefully pour some Chromium Etchant in the first beaker/envelope such that it will cover your sample.
4. Fill the other two beaker/envelopes with DI water such that it will cover your sample. DI water is used for rinsing the etchant.
5. Calculate the etch time for your sample. You will need to know the thickness of your chromium layer. At 25°C, the Cr will etch at a rate of approximately 60 nm/min. This may not be exact! It is recommended to test this for yourself.
6. Put your sample into the etchant and move your sample for the appropriate amount of time calculated in the previous step. *If etchant at the surface becomes saturated and fresh etchant cannot reach the surface, then etching will slow down. Agitation can be used to bring etchant to the surface and promote etching.* In this case use a magnetic stirrer and carefully swirl your etchant to accelerate the etch and improve uniformity.

#### DI Water rinse

1. When the etch is complete, transfer the sample carefully to the first DI water rinse beaker/envelope and move the sample for 5 minutes in DI water.
2. If you use tweezers to move the sample, make sure you rinse your tweezers as well.
3. Transfer the sample to the second DI rinse beaker, and rinse for another 5 minutes while moving your sample.

#### Sample dry

1. After the water rinse is finished, remove your samples and blow them dry with the N<sub>2</sub> gun.
2. After getting most of the water off, it is optional to dry the samples in an oven at 120 °C or on a hotplate at 150 °C.
3. Inspect wafer for traces un-etched chromium. If features are small, use an optical microscope. If more etch time is required, place wafer back into the beaker with the etchant for another 30 seconds while swirling. Repeat rinse and drying procedure.

#### Clean-up

1. Let the etchant cool down to room temperature.
2. When the used etchant is at room temperature, pour it carefully over the other two beakers/envelopes filled with DI water.
3. Fill the beaker where you had your etchant with DI water.

4. Use the venturi to remove the waste from all the beakers/envelopes.
5. Rinse all the beakers/envelopes three times with DI water.
6. Turn all the beakers/envelopes upside down, wash the outside with DI water and blow them dry with the N<sub>2</sub> gun.
7. Return all labware to its proper location.
8. Clean the area and rinse it with DI water.
9. Wash your black gloves and leave them in the bench.

## 5. Primary Hazards

This material is corrosive to the eyes, skin and mucous membranes and causes irritation and burns. Vapours severely irritate the respiratory track. Do not mix with strong oxidants or organic material and do not heat.

## 6. Engineering Controls to Prevent and Mitigate Hazards

Carry out the procedure in a wet bench. Store bottles of chemicals (sealed tightly) in cabinets in the inorganic cabinets. Work area should contain an eye wash, safety shower and a bottle of diphoterine. Check where you can find this in your neighbourhood.

The chemicals are in the medium risk category:

- Processing during afterhours requires the presence of a buddy, mixing of chemicals is not allowed (prepare your solution beforehand) and the maximum quantity of liquid is 100 ml.
- If one of these points is not fulfilled the process is considered to be high risk and it must be done during office hours.

## 7. First Aid and Emergency Procedures

Eye Contact: Immediately flush with diphoterine while lifting upper and lower eyelids occasionally (use the complete 500 ml for one eye and remove contact lenses if possible). After using diphoterine, flush with water for at least 15 minutes. Get immediate medical attention. Press the evacuation button.

Skin Contact: Remove contaminated clothing, wash skin with diphoterine. After using diphoterine, wash with water. If there is any irritation, get medical attention. Press the evacuation button.

Inhalation: Remove to fresh air. Resuscitate if necessary. Take care not to inhale any fumes released from the victim's lungs. The quick response team has to use the "Eerste Hulp Zuurstof Tas". Get immediate medical attention. Press the evacuation button.

Ingestion: Do not induce vomiting. Get immediate medical attention. Press the evacuation button.

In case of a spill: Press the evacuation button.

In case of a fire: Press the fire button. Use the CO<sub>2</sub> extinguisher to extinguish the fire.

## 8. Literature

- [1] Microchemicals, "Chromium Etching," 7 November 2013. [Online]. Available: [https://microchemicals.com/technical\\_information/chromium\\_etching.pdf](https://microchemicals.com/technical_information/chromium_etching.pdf). [Accessed 2018].